B. Electrochem 4(11) November 1988, pp 965-967

ELECTROCHEMICAL BEHAVIOUR OF CATALYTIC HYDROGEN CATHODES IN ALKALINE SOLUTIONS

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[Received: 1987 February; Accepted: 1988 September]

Alloy coatings of Ni-Mo, Ni-Co-S and Ni-Co-W were prepared by electroplating on nickel plated mild steel substrate. The coatings exhibited fairly good electrocatalytic activity for hydrogen evolution in the range of 70-100 mV in 30wt% NaOH at 353K when a constant current density of 3kA. m^{-2} was applied. But the cathode potential increased with time, indicating that the coating is gradually getting deactivated during prolonged operation.

Key words: Electrocatalyst, hydrogen overvoltage, chlor-alkali

INTRODUCTION

Over the past few years, several developments have taken place which contributed to a significant reduction in the energy requirement for the electrolytic production of caustic soda-chlorine. These developments include: new and improved cell designs, coated titanium anodes, modified diaphragms and membrane cell technology. However, a 0.3-0.4V overpotential is still experienced on the cathodes for the hydrogen evolution reaction in non-mercury chlor-alkali cells. Any reduction in this cathodic overvoltage will result in substantial saving in electrical energy.

Our research efforts are aimed at the development of a suitable catalytic hydrogen cathode with low hydrogen overvoltage and fairly long service life in chlor-alkali cells. Hydrogen evolution reaction has been extensively studied in the past 100 years and the catalytic effect of the electrode material upon its rate is well documented in the literature. It was pointed out that the catalytic activity of the metals for the hydrogen evolution reaction is a periodic function of atomic number within the three long transition periods [1]. The exchange current density is a measure of such activity. The electronic configuration of outer shells of elements in their ground state shows that the catalytic activity first increases with the increase of the d-electrons, reaches its maximum at a nearly filled d- orbital, sharply decreases after its completion with one or two electrons in the s-orbital and then increases again with successive addition of electrons to the p and subsequent d-orbitals. Earlier workers [2,3] showed that hydrogen overvoltage at constant current density in alkaline solutions varied periodically with the atomic number of the electrode materials. A volcano-type curve was observed to exist in the dependence of the logarithm of exchange current density on the intermediate metal-hydrogen bond strengths[4]. The precious metals lie at the peak, with metals that form weak M-H bonds (generally sp metals) on the ascending branch and metals that strongly adsorb hydrogen on the descending branch of the curve.

It was suggested that an ideal electrocatalyst for the hydrogen evolution reaction should require two electrons to fill its outer d and s orbitals, have a work function of 5 eV and form a M-H bond of about 50K. cals $mole^{-1}$ [2,3]. The most widely investigated electrocatalysts are coplated transition metals. Some of the results given in the open literature show that the best activity is achieved with coplated transition metals. In the present work, electrocatalysts were prepared by combining either Ni or Co which form on the ascending part of the volcano curve with either Mo or W which fall on the descending part of the curve and their morphology and polarization behaviour were studied.

EXPERIMENTAL

Mild steel, stainless steel (Grade 316), nickel plated mild steel were used as substrate for the plating. To minimise edge effects, cutting edges were machined properly. Pretreatment procedures were varied depending on the substrate. Mild steel substrates were cathodically cleaned in an alkaline bath containing NaOH, sodium silicate, sodium phosphate at 353K at a current density of 100 $mA.cm^{-2}$ and were given a dip in 20% sulphuric acid prior to immersion in the plating bath. Stainless steel substrates were etched in hot HCl for 10 mins. In the case of nickel plated m.s., m.s. strips were electroplated from a Watt's nickel bath and they were transferred directly to the alloy plating bath without washing. In electroplating baths two, thin, smooth and rectangular graphite plates covered in a bag of nylon cloth were used as anodes. Details of the electroplating baths are given in Table I.

TABLE-I: Electroplating baths

Alloy	Bath composition		Plating conditions
Ni-Co-S	$NiSO_4.6H_2O$:	263 gpl	C.d.:50-190 mA. cm^{-2}
	$NiCl_2.6H_2O$	: 47.5 gpl	Temp. : 313-323K
	$CoCl_2.6H_2O$	: 95 gpl	Plating time: 1 hour
	H_3BO_3	: 30 gpl	
	KCNS	: 30 gpl	
Ni-Co-W	$NiCl_2.6H_2O$	: 118.85 gpl	C.d. : 60 mA. cm^{-2}
	$CoCl_2.6H_2O$	: 23.8 gpl	Temp. 333K
	$Na_2WO_4.2H_2O$	: 66 gpl	Plating time:1 hour
	$Na_4P_2O_7.10H_2O$	:446 gpl	
	pH	: 8-9	
Ni-Mo	$NiSO_4.6H_2O$	: 58 gpl	C.d: 50 mA. cm^{-2}
	$Na_2MoO_4.2H_2O$	:12 gpl	Temp. : 303K
	NaK tartrate	: 76 gpl	Plating time:1 hour
	NaCl	: 10 gpl	
	(NH_4OH)	: To make pH = 10	

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The surface morphology of the coatings were analysed by a scanning electron microscope (SEM) at a magnification of 500 X. Chemical composition of the deposits were analysed by the EPMA attached to SEM. The average deposition thickness was measured using a micro test thickness measuring meter.

Galvanostatic polarisation measurements were carried out in steady state. A d.c. constant current power supply was used to control the polarisation currents precisely and a digital voltmeter to measure electrode potentials. A cylindrical stainless steel tank of capacity 3 litres was used as the electrolytic cell. The cell was filled with 2 litres of 30% (400 gpl) sodium hydroxide solution prepared using analar grade sodium hydroxide pellets and triple distilled water. The electrolyte was continuously stirred by means of a motorised stirrer. Two electrolytic grade nickel plates of large area placed in a bag of nylon cloth were used as anodes, one on each side of the deposited cathode. Hg/HgO, OH^- electrode was used as reference electrode. The luggin capillary of the reference electrode was kept positioned at 0.1 mm from the surface of the working electrode. Potentials were recorded after waiting for a standard time of 30 secs at each current. Potentials were measured and reported vs Hg/HgO, OH^-. The correction for IR drop for the resistance of the electrolyte between the working electrode surface and the luggin capillary was not done.

RESULTS AND DISCUSSION

Average thickness of the coating was of the order of 10 μm. The surface of the deposits were fairly smooth and strongly adherent. The colour of deposits varied from grey to black depending on the constituents of the alloys deposited.

Galvanostatic polarisation studies revealed that overpotential for H_2 evolution on these electrodes ranges from 80 to 130mV at a current density of 300 mA. cm^{-2} in 30% NaOH solution at 353K. Fig. 1 shows current density-potential plots for the different alloy deposits. The increase in overpotential for an increase of current density from 50 to 300 mA. cm^{-2} was only of the order of 30 to 80 mV. This behaviour indicated that all the deposits tested had excellent electrocatalytic activity for the hydrogen evolution reaction. Accelerated life tests carried out using these electrodes in 30% sodium hydroxide solution at 353K at a current density of 300 mA. cm^{-2} made it clear that these electrodes lacked long term stability required for commercial exploitation. Cathode potential increased steadily with time, indicating that the coating is gradually getting deactivated during operation. Mild gas evolution was observed in almost all cases even when the electrode was in open circuit. In the case of Ni-Co-S electrode, on open circiut, the colour of the solution in the vicinity of the electrode turned blue which may be due to Co becoming anodic with respect to nickel and the consequent preferential dissolution of Co. None of the coatings withstood the accelerated life test beyond 200 hours. It is worthwhile to mention here that catalytic cathodes are technically viable only when their coating life is of the order of 1.5-2 years.

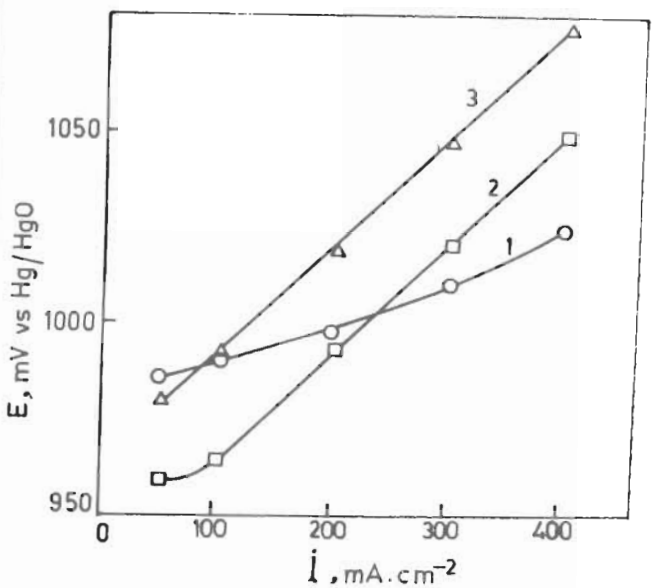

Fig.1: i-E curves for different coated cathodes in 30 wt% NaOH solution at 353K (i) Ni-Mo (ii) Ni-Co-S (iii) Ni-Co-W

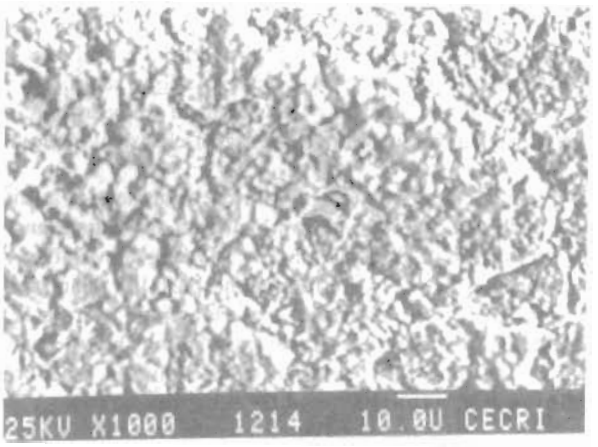

Fig.2(a) SEM photomicrograph of Ni-Mo coating

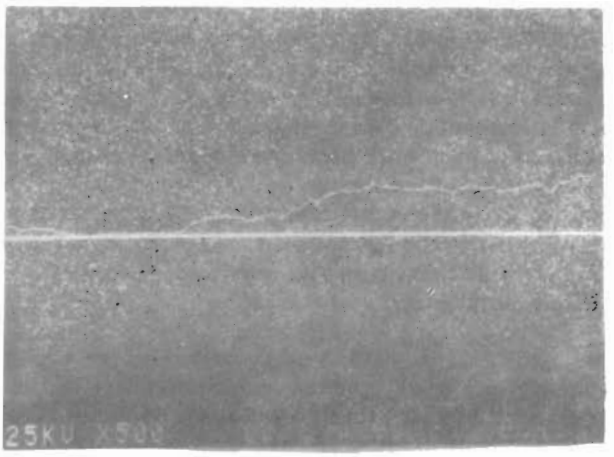

Fig.2(b) SEM-mapping for nickel

Examination of the scanning electron micrograph of the surface of the deposits revealed that by and large the deposits were very smooth and strongly adherent. Fig. 2(a) shows the scanning electron micrograph of a typical Ni-Mo deposited surface. Mapping of the constituent of the deposited alloy EPMA indicated that the constituents of the alloy were not uniformly distributed over the surface of the substrate and the substrate is exposed in patches. Figs. 2(b) and 2(c) depict typical nickel and Mo mapping of the alloy deposited surfaces respectively. These observations imply that the destabilisation of the electrocatalyst may be due to hydrogen evolution on the substrate or the constituents of the electrocatalyst not forming a homogeneous single phase solid solution, but present as separate phase offering sites for hydrogen evolution.

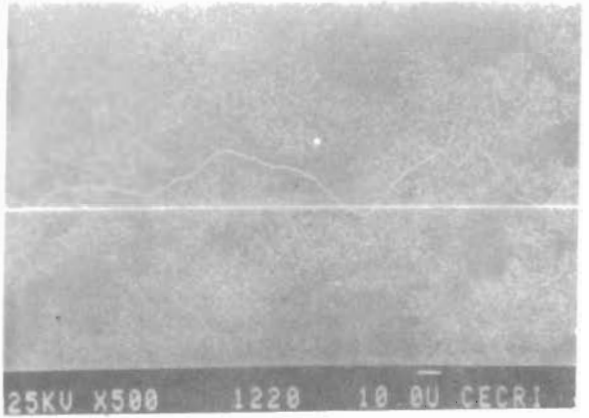

Fig.2(c) SEM-mapping for molybdenum

CONCLUSION

Though coplated transition metals are excellent electrocatalysts for hydrogen evolution reaction, they lack the long term stability required for usage in chlor-alkali cells. Now attempts are being made to prepare precious metal/metal oxide incorporated cathodes; so that H_2 evolution takes place only on catalytically stabilised sites and not on the substrate. These cathodes are in continuous operation for the past few months in the actual working condition of the chlor-alkali cell with a constant overvoltage of 70-80 mV.

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